

LA-UR -76-2279

WASER

CONF-770301--1

TITLE: ELECTRON MICROPROBE STUDIES OF MAHOGANY ZONE AND DEVONIAN SHALE.

AUTHOR(S): E. A. Hakkila, R. E. Elliott, J. M. Williams
and E. M. Wewerka

SUBMITTED TO: Symposium on Analytical Chemistry of Tar Sands
and Oil Shales, American Chemical Society,
March 20-25, 1977

By acceptance of this article for publication, the publisher recognizes the Government's (license) rights in any copyright and the Government and its authorized representatives have unrestricted right to reproduce in whole or in part said article under any copyright secured by the publisher.

The Los Alamos Scientific Laboratory requests that the publisher identify this article as work performed under the auspices of the USERDA.


los alamos
scientific laboratory
of the University of California
LOS ALAMOS, NEW MEXICO 87544

An Affirmative Action/Equal Opportunity Employer

NOTICE
This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights.

SYMPOSIUM ON ANALYTICAL CHEMISTRY OF TAR SANDS AND OIL SHALES
PRESENTED BEFORE THE DIVISIONS OF ANALYTICAL CHEMISTRY AND PETROLEUM CHEMISTRY, INC.
AMERICAN CHEMICAL SOCIETY
NEW ORLEANS MEETING, MARCH 20-25, 1977

ELECTRON MICROPROBE STUDIES
OF
MAHOGANY ZONE AND DEVONIAN OIL SHALES

by
E. A. HAKKILA, N. E. ELLIOTT,
J. M. WILLIAMS AND E. M. WEWERKA

1.0 INTRODUCTION

The energy crisis, brought about by dwindling oil and gas reserves, has caused our nation to seek new sources of these strategic commodities. Among the possible oil and gas sources are the Green River shales of the Rocky Mountains and the Devonian shales in the Eastern U.S. The organic matter (kerogen) in the Green River shale is the potential source of over 4 trillion barrels of oil or petroleum feed stock. Entrapped within the Devonian shale is a huge resource (over 500 quadrillion cubic feet) of natural gas. Unfortunately, the resources in both these deposits are contained in rock matrices, and extraction of the oil or gas from either of these shale beds is costly and very difficult.

While some efforts are underway to increase production efficiency, others have been directed at characterizing the rock matrices to determine how and where the resources are contained. This knowledge will be useful in deciding where and how the reserves should be released. The purpose of this study is to demonstrate the utility of the electron microprobe in characterizing both Western and Devonian shales. For this purpose, we have chosen samples from each of the shale zones mentioned. The studies reported have just begun, but do allow some initial comments about similarities and differences between the shales and some speculation about their formation.

2.0 INSTRUMENTATION AND PROCEDURE

One sample each of Green River and Devonian shales were obtained, respectively, from the Laramie and Morgantown Energy Research Centers. The Green River shale was taken from the Mahogany Zone in the Piceance Basin of Colorado and the Devonian specimen was taken from the 800-meter depth of the Marcelus Layer, Consolidated Gas Well No. 9041 in Jackson County, WV. Each sample was sectioned as a slab, 2.5 to 3.0 cm long and 1.2 cm wide by 0.6 cm thick, with the long direction parallel to the vertical direction of the core. The samples were polished to reveal the microstructure, and then coated with a 100 Å layer of carbon to provide electrical conductivity.

The electron microprobe used in this study was an Applied Research Laboratories Model EMX-SM, equipped with three x-ray spectrometers of differing wavelength capabilities. This arrangement allowed all elements heavier than beryllium

to be studied. The spectrometers, stage motion (x- or y-directions), and scaler-timer readout were controlled manually or through a PDP-8E computer. A secondary electron detector permitted scanning electron micrographs to be taken. These SEM photographs allowed the two-dimensional x-ray images of elemental distributions to be correlated with surface features.

Two techniques were used to obtain information on sample composition. In the first, the electron beam was rastered rapidly over a specified area (here 80 by 100 μm) and the characteristic x-rays of the elements sought were monitored. An x-ray intensity ratio for each element in the entire area was determined from the intensity of the x-rays versus those from a standard material: pure iron for Fe, pyrite for S, pure aluminum for Al, a grossularite for Ca, and graphite for C. By sweeping many adjacent areas, detailed information about the microscopic changes in elemental and mineral composition across a sample could be obtained. In the second technique, the electron beam was rastered slowly across a preselected area of the sample, and the intensities of the elements of interest were recorded photographically from an oscilloscope screen. This method provided point-by-point information about the elements present and rough estimates of their relative concentrations. Data from the microprobe analyses were correlated to previously published mineralogical studies on the Mahogany zone shale (1).

3.0 ANALYTICAL RESULTS

3.1 Mahogany Zone Shale

Light and dark banding in the Mahogany Zone shale is shown in the photomicrograph of Figure 1. Using the rapid rastering technique, intensities for Fe, S, Ca, Al, and C were determined along the complete 3-cm length of the specimen and the intensity ratios plotted in Figure 1. The low, C x-ray intensities of the tan bands are indicative of material that is depleted in organic matter. These light bands are primarily carbonates and contain less S and Al and more Ca and Fe than the dark, C-rich bands. The changes in Fe intensities are much more pronounced than changes in Ca intensities. The sharp spikes in the S intensities are associated with areas of high pyrite concentration, as evidenced by comparable Fe spikes. The pyritic areas are associated with the organic-rich bands. A notable exception to the Fe-S association is the S spike at approximately 16,000 μm which is not accompanied by a corresponding rise in the Fe intensity. This region includes a very dense organic strip and is discussed below (area C). Three areas of the sample were examined in detail using the second microprobe technique. Area A was a dark band near the 6000 μm position in Figure 1. Area B was in the wide, light tan area at approximately 13,000 μm , and Area C included the black, organic strip at approximately 16,000 μm . Observations made in these areas are presented in the following paragraphs.

A scanning electron micrograph (SEM) and corresponding element intensity scans for area A are shown in Figure 2. This area contains numerous, metallic-appearing particles. These particles appear as the light, often angular, crystals in the SEM. They contain only S and Fe in detectable concentrations, and are probably pyrite. At least three other minerals are also present in this area. A phase that appears fine-grained in the SEM contains predominately

Ca, Mg, C, and O and small amounts of Fe, and is probably dolomite. The large circular grains in the SEM contain predominately Al, Si, Na, and O and may be albite. Potassium is associated with aluminum in a fine-grained, silicate phase which is probably illite.

Area B is in the light tan strip on either side of the crack at approximately 13,000 μm on the photomicrograph in Figure 1. This area is characterized by a significantly higher Fe concentration than in the darker areas of the sample. The Fe is associated with Mg, C, and O and lesser amounts of Ca, and probably occurs as a Fe-rich dolomite or ferroan. Between grains of this material is a mineral that contains Al, Si, K, and O and is probably illite. Another mineral phase contains Al, Si, and O, but no K or Na, and is probably kaolinite or montmorillonite. Quartz and TiO_2 are also present in minor amounts in this area.

Area C contains a black strip which contains predominantly C, but also contains significant amounts of Na, S, and O. The S is probably organic, as indicated by the shape of the K-beta, x-ray bands (2). A dolomitic phase, containing less Fe and Mg than found in Area B, and a silicate phase, containing Al and K, are heterogeneously distributed around the black strip. Small inclusions, generally less than 5 μm in diameter, contain Ti and O and appear outside of the black strip.

3.2 Devonian Shale

The Devonian shale sample generally had a darker appearance with fewer and less distinct bands than did the Mahogany Zone shale, and the organic matter appeared to be more evenly distributed over the 2.5-cm sample. Several areas were examined using the second probe technique to identify the minerals present. Observations made in these areas are presented in the next few paragraphs.

Area A is in one of the dark areas and contains numerous, metallic-appearing particles, as well as black, irregularly shaped, carbonaceous matter. The metallic-like particles, as in all other areas examined, contained only Fe and S and are probably pyrite. The organic matter is generally surrounded by siliceous material consisting of SiO_2 and Al-silicates which contain only minor concentrations of K. One unusual particle contains Ti which is apparently associated with C rather than O.

Area B is near one of the dark bands and contains a carbonate phase whose metal component is predominantly Fe. Since only low concentrations of Mg and no Ca are observed, the material is probably siderite. An organic phase contains low concentrations of Ca. An unusual, round particle, approximately 25 to 30 μm in diameter, consists of Ca, P, and O and is probably an apatite.

Area C is shown in Figure 3 and is in one of the darker, organic-rich bands. (Note that the photomicrograph is the mirror-image of the SEM and x-ray photographs.) The areas that appear black in these photos contain the carbon-rich, organic matter. The matrix contains Si, primarily as quartz, but also as Al-silicates with low concentrations of K. Two distinct carbonate phases can be differentiated. One in the upper right in the SEM contains predominantly Fe with lesser amounts of Mg and only small amounts of Ca, and is probably siderite or ferroan. The second carbonate phase is more

widely spread at the right and contains predominantly Ca with lesser amounts of Fe and Mg. The large, irregularly shaped particle at the left center of the SEM contains Ti and O.

This sample, after polishing, was covered with a cap. When the cap was removed, small droplets of liquid were observed on the surface. On exposure to dry air, the liquid disappeared leaving small cubic crystals of Na and Cl. Presumably, these elements were leached from the interior of the sample.

4.0 DISCUSSION

This study was performed to demonstrate the utility of an electron microprobe-SEM in elucidating the structures of energy-bearing shales. The microprobe produces a large volume of detailed information in a relatively short time. The mineral analyses reported here are qualitative, but quantitative identifications are available to more clearly identify minerals (3). The qualitative data, however, when correlated with mineralogical studies, do allow rapid analyses of the structure of shales. The data obtained in this study provided several implications about structural relationships.

The Mahogany Zone and Devonian shales have distinct dark and light bands which reflect the sedimentary nature by which the shales were formed. These bands vary from less than 50 μ m thick, to as much as several mm. Thus, while the entire shale forming periods were long - the Mahogany Zone is over 500 meters thick in some spots and the Devonian shales are over 1200 meters thick in some places - each band forming period was rather minuscule. The Devonian shale bands are less pronounced and wider and were likely to have been formed under less static conditions over a longer period of time or at a faster, but less selective, rate than were the Mahogany Zone bands. Depending upon the geological conditions, organic matter would be included in the sediments. The dark bands in both shales were found to possess this organic matter, while the light ones did not.

Both the Green River and Devonian shales are basically carbonate-silicate formations which require neutral or alkaline conditions to form. Smith (1) has suggested that the Green River shales were formed at pH levels between 8.5 and 10. The carbonate types typically encountered are calcite (calcium), dolomite (calcium, magnesium), ferroan (magnesium, iron) and siderite (iron). All these species were observed in both of the shales, but the Devonian shale had regions with much higher concentrations of iron (siderite) than were found in the Mahogany Zone shale. This would imply that either the iron content in the Devonian shale environment was higher than that in the Mahogany Zone or that the conditions in the Mahogany Zone were not as conducive to iron precipitation. Siderite solubility for example, increases in alkaline solution, particularly in the presence of dissolved carbonates (4).

Smith (1) also reasoned that the presence of organic matter should enhance the precipitation of silicate minerals. Our data corroborates this postulation. Thus, we find that the organic-rich bands in both the Mahogany Zone and Devonian shales have higher concentrations of siliceous minerals than do the organic-deficient bands. These siliceous minerals occur as quartz and as aluminosilicates.

Mason (5) reports that clay mineral formation is governed by pH. Thus, as alkalinity increases, clay formation shifts from kaolinite to montmorillonite to illite. This series reflects increasing amounts of silicon and potassium relative to aluminum. The much higher concentrations of potassium which were observed in the Mahogany Zone shale would indicate that it was formed in a more alkaline environment than was the Devonian shale. The potassium clay minerals were observed to be very finely dispersed in both samples. This suggests that they were probably formed concurrently with the organic precipitates. Interestingly, the sodium-aluminum silicates sometimes appeared as large grains. No divalent ions (calcium, magnesium, or iron) were found in the aluminosilicates, suggesting epigenetic formation of the latter.

Relatively large negative Eh values (reducing conditions) have been predicted for the formation of the Mahogany zone shales (1). The observation that none of the sulfur present in either shale was observed as sulfate would corroborate this. Most of the sulfur in both cases appears as FeS_2 , and is more likely pyrite than marcasite which forms only under more acidic conditions. The pyrite particles generally are less than 50 μm in diameter, indicating that prevailing conditions did not permit significant crystal growth. Most of the pyrite was observed in or adjacent to the organic-rich areas. The source of the S in the samples is not known. It could have been introduced as sulfate in the form of gypsum, with subsequent dissolution and reduction to sulfide under the strong reducing conditions in the organic-rich zones. Bradley (6) in a discussion of the formation of algal sediments in a Florida lake reported the presence of 0.5 to 1% of sulfur in the organic sediments of blue-green algae. This source could account for the presence of organic sulfur in the Mahogany shale kerogen bands.

Several other minerals were also observed in both shale samples. These were TiO_2 and apatite or fluoroapatite. Sodium chloride was also observed in the Devonian shale, but not in the Mahogany Zone specimen.

This study was not intended to be a definitive microprobe comparison or examination of the two shales, but, rather, it was intended to demonstrate the utility of the microprobe in studying energy-bearing shales. Consequently, much more work is needed to identify the clay minerals better and to determine the nature of the minuscule deposit-layers. Also no attempt was made to locate trace elements, other than to note that certain rare earth elements - Ce, La, and Pr - are concentrated in the apatite grains of the Mahogany Zone shale. These and other problems will be clarified only when additional studies are undertaken.

5.0 ACKNOWLEDGMENT

We thank the Laramie (LERC) and Morgantown (MERC) Energy Research Centers for providing us with shale samples. We also thank Dr. John Ward Smith of LERC for pointing out the need for these characterization studies and for his encouragement and helpful discussions.

6.0 REFERENCES

- (1) Smith, J. Ward, Rocky Mountain Association of Geologists, 1974 Guide-book, pp. 71-79.
- (2) Hurley, R. G., and E. W. White, Anal. Chem. 46, 2234-2237 (1974).
- (3) Bence, A. E., and A. L. Albee, J. Geol. 76, 382-403 (1968).
- (4) Mellor, J. W., "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. XIV, Longmans, Green, and Co., New York (1953), pp. 355-369.
- (5) Mason, Brian, "Principles of Geochemistry," 2nd Ed., John Wiley and Sons, New York (1958), p. 154.
- (6) Bradley, W. H., Geol. Soc. of America Bull. 81, 985 (1970).

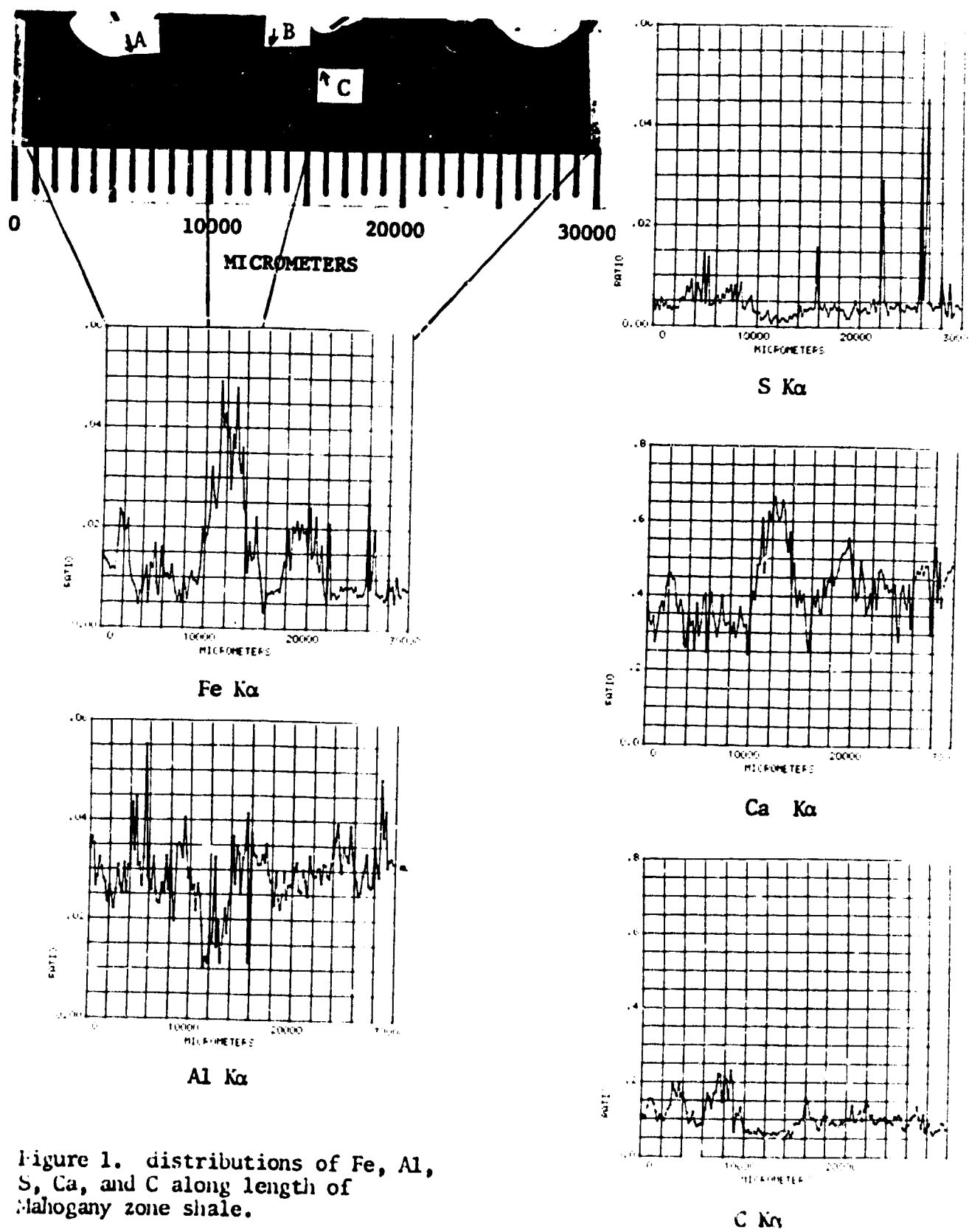


Figure 1. distributions of Fe, Al, S, Ca, and C along length of Mahogany zone shale.

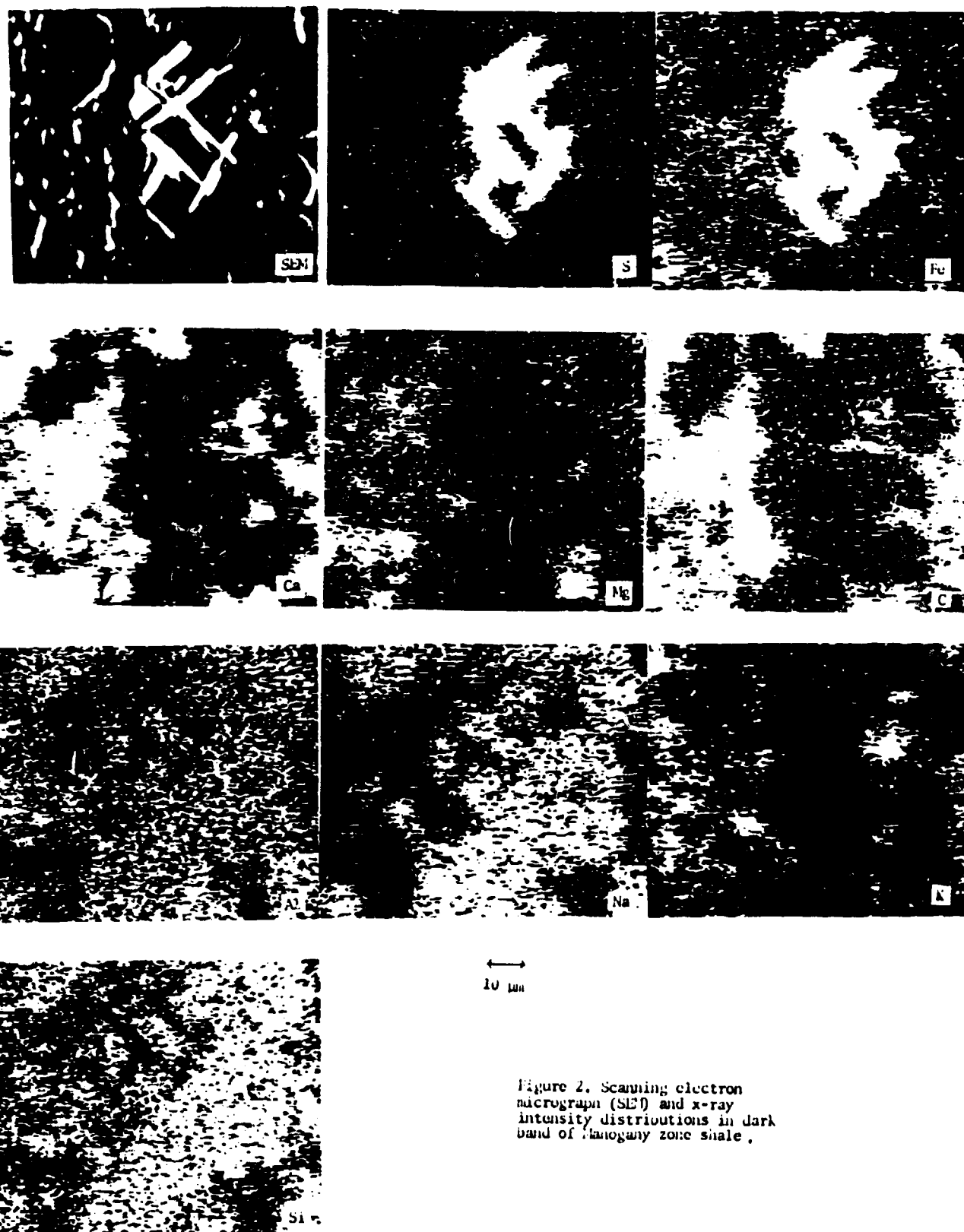


Figure 2. Scanning electron
micrograph (SEM) and x-ray
intensity distributions in dark
band of Manogany zone shale.

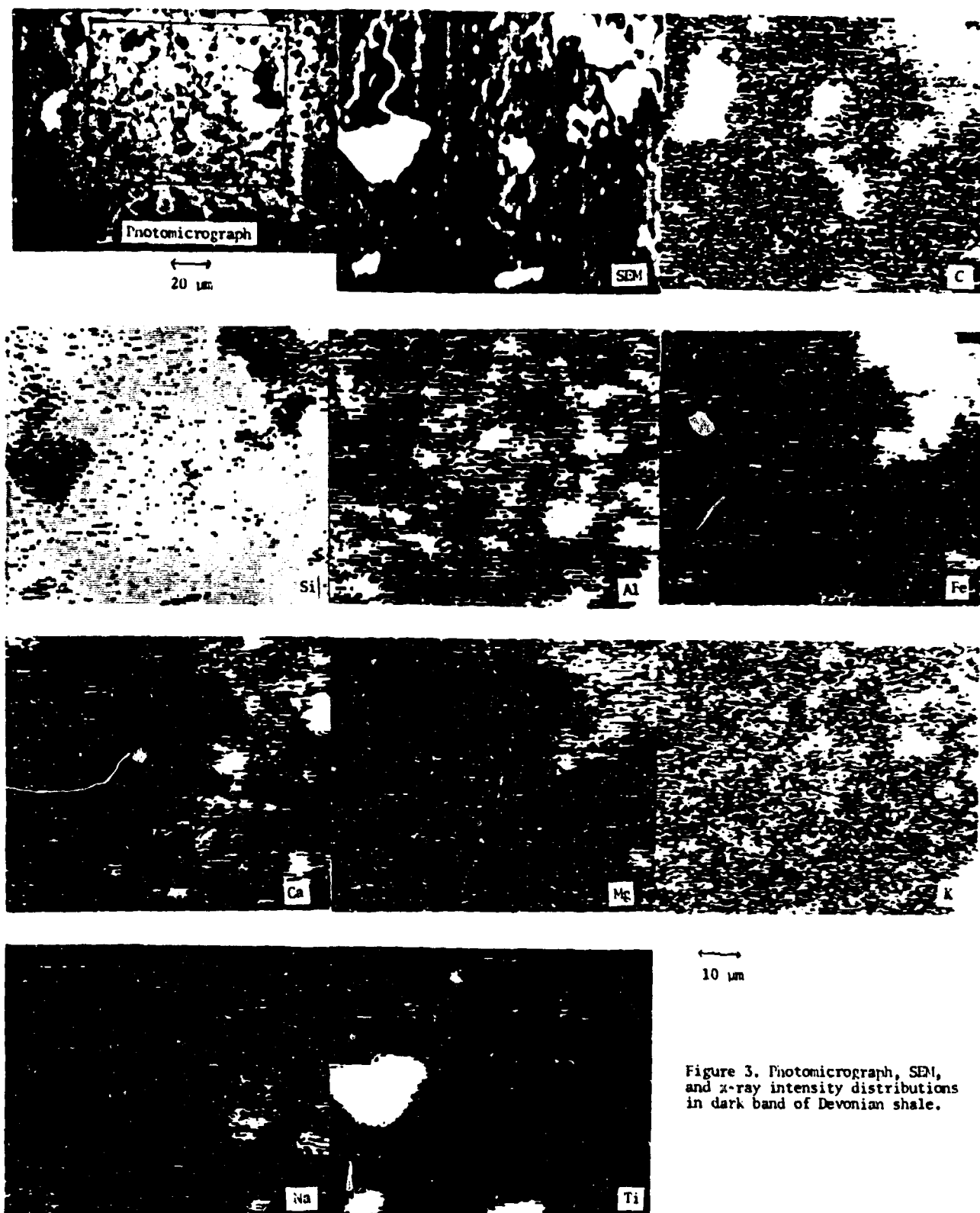


Figure 3. Photomicrograph, SEM, and x-ray intensity distributions in dark band of Devonian shale.